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The Preparation and Properties of Polymer/Nanoparticle Blends Using POSS™

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Spe oligo

The synthesis of nanoparticle/polymer blends has expanded greatly in recent years. When the nanoparticles are ceramic, these blend materials have the advantage of combining a ceramic type material with an organic polymer that can result in a material that may bridge the performance gap between the two systems. Our labs have been working with Polyhedral Oligosilsesquioxanes (POSS™) to enhance the performance characteristics of polymers. One aspect of this program is the preparation of POSS™/polymer materials using traditional blending techniques. We have shown that simply changing the organic functionality around the POSS™ molecule can lead to POSS™ dispersion in a wide array of polymers, including polyethylene, polypropylene, polystyrene, polycarbonate, SB rubber, and many other polymers. In several cases we have been able to maintain clarity of the polymer after dispersion. The synthesis of POSS™/polymer blends and the observed property enhancements of the POSS™/polymer blends will also be discussed.

Introduction

The synthesis of organic polymer/inorganic ceramic hybrid materials has become a very popular research topic in recent years. The primary goal of this work is to generate new materials that meld together the best properties of ceramics (high temperature stability and durability) and plastics (flexibility, processability) and bridge the performance gap between the two systems[1].

Polyhedral Oligomeric Silsesquioxanes (POSS™) can be thought of as well-defined silica particles with an outer coating of organic material. This organic material serves two purposes: first, it acts as a passivating layer so the silica particles do not agglomerate; and, second, it serves as a compatiblizer with the polymer matrix. POSS™ was originally synthesized by the controlled hydrolysis of alkyl trichlorosilanes in an organic solvent. Depending on the organic side group and the specific conditions (solvent, concentration, temperature, etc.), incompletely condensed materials or fully condensed materials can be formed.

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Previous research has shown that such hybrid systems can be prepared by incorporating polyhedral oligosilsesquioxanes (POSS™) into traditional organic polymers (polymethacrylate, polystyrene, polynorbornene)[2] by standard polymer preparation procedures. The development of each of these systems was not trivial, with development times of about a year. However, when the POSS™ is physically attached to the polymer chain, property enhancements are invariably observed. Also, dispersion of the POSS™ into the polymer is possible regardless of the R group surrounding the POSS™ molecule. For example, a film of a physical blend of 10% cyclopentylPOSS™ (Cyclopentyl$_8$T$_8$, see equation below) in polymethacrylate is opaque, while a film of polymethacrylate with 10% of CyclopentylPOSS™ methacrylate physically attached to the polymer chain is optically clear.

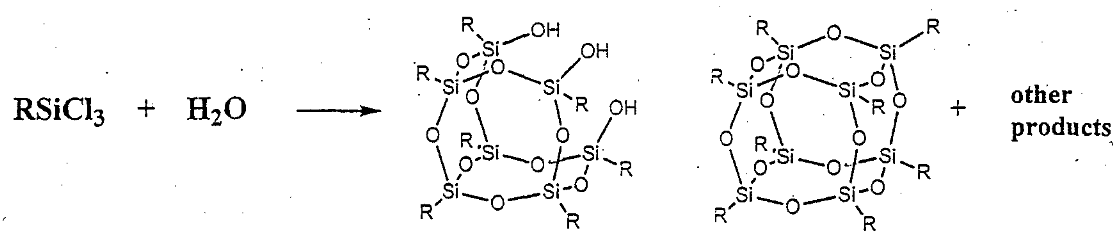
A more convenient method of incorporating POSS™ into an organic polymer is to blend it into the polymer. With this method of POSS™ incorporation, there would be no covalent linkage between the POSS™ molecules and the polymer. The resulting hybrid material would not have the same properties as a POSS™ hybrid with a covalent linkage to the polymer and would more likely act like a filled polymer system. Also, the preparation of POSS™ polymer blends is very straightforward, using traditional blending techniques. Since an individual POSS™ molecule is a chemically distinct

nanostructured™ species, there is only one possible size of 15Å which includes the organic side groups. In order to make a blend that maximizes property enhancements of the hybrid material, it is believed that the silsesquioxane should be evenly dispersed in the polymer at the molecular level. Since each POSS™ molecule has a Si_8O_{12} core covered with alterable organic side groups, it is believed that a finer dispersion into the polymer matrix may be possible by increased interaction of compatible side groups and the polymer.

POSS™ Monomer Development

Critical to the success of this work is the availability of POSS™ monomers with many different side groups. Completely condensed POSS™ compounds have been known for quite some time, with $methyl_8T_8$ and $phenyl_8T_8$ being two of the oldest. Incompletely condensed materials are relatively new, with the preparation of $Cyclohexyl_7T_7(OH)_3$ by Brown and Vogt in 1965. The synthesis of this material took extended periods of time, with gestation periods of at least three months to obtain multigram quantities of a mixture which then required a time consuming purification procedure to isolate the final product. Attempts at accelerating the reaction by heating the solvent led to the formation of the completely condensed $cyclohexyl_6T_6$. Fortunately, in 1991, Feher et al[3] discovered that:

Is this what they discovered? Or is Cyclopentyl the continuation of the sentence? If it's the latter, the "C" should be lower case.



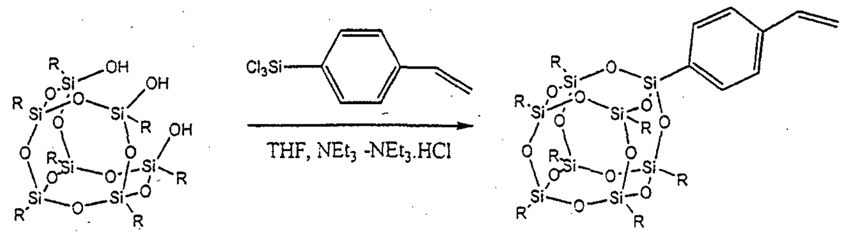
R = cyclopentyl
cyclohexyl
vinyl

R = cyclopentyl
cyclohexyl

R = cyclopentyl (1)
vinyl (2)

$Cyclopentyl_7T_7(OH)_3$ can be prepared in multigram quantities in three days by refluxing the $cyclopentylSiCl_3/H_2O$/acetone reaction solution. Moreover, the isolation of the material was as simple as filtering and drying. In 1994, ~~the~~ Lichtenhan, et al, further refined the process so that kilogram quantities of $Cyclopentyl_7T_7(OH)_3$ were synthesized.

Lichtenhan also pioneered the synthesis of corner capping incompletely condensed silanols with reactive groups with the specific purpose of polymerizing/grafting the POSS™ molecules into polymers. For example, $Cyclopentyl_7T_8Styryl$ (**3**) is synthesized by the addition of $styrylSiCl_3$ to triol $cyclopentyl_7T_7(OH)_3$ in the presence of triethylamine to absorb the HCl generated. This material can then be copolymerized with styrene to give a POSS™-polystyrene copolymer.



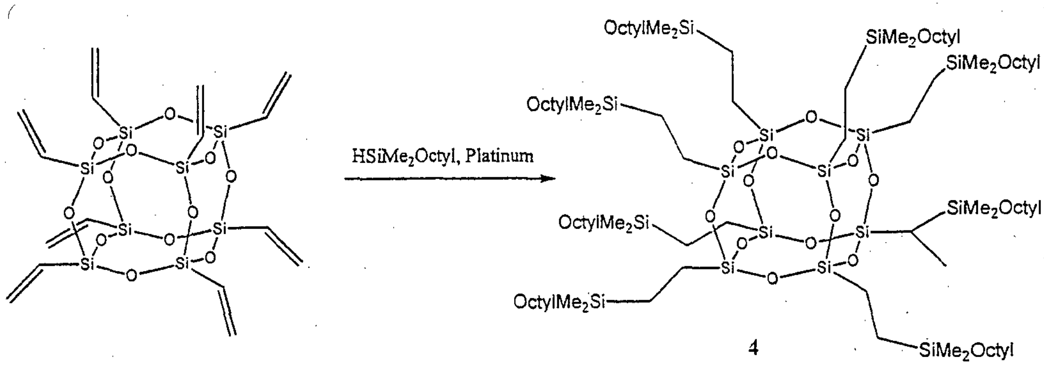
R = cyclopentyl

R = cyclopentyl (3)

Another POSS™ compound utilized by Lichtenhan and the Air Force is vinylPOSS (2). This material was originally made by the hydrolysis of vinyl$SiCl_3$ in an ethanol/water solution, with a dismal yield of 20%. After the POSS™ technology was transferred to the private sector, Hybrid Plastics invented a new process to synthesize a multifunctional vinylPOSS™ material in higher yield and therefore at a lower cost than vinyl$_8T_8$ (2). The new vinylPOSS™ material (vinyl$_nT_n$) is a mixture of octameric vinyl$_8T_8$ (2), decameric vinyl$_{10}T_{10}$, and dodecameric vinyl$_{12}T_{12}$. The reaction chemistry between vinyl$_8T_8$ and the vinylPOSS™ mixture is identical and can practically be used as a drop in replacement for vinyl$_8T_8$. (add a space)

Hydrosilation of POSS™

Some of the first polymers into which we wanted to blend POSS™ ~~into~~ were high density polyethylene and polypropylene. Since some additives used for HDPE use long chains to compatiblize the additive with the polymer matrix, a similar approach was used for POSS™. Since no long chain hydrocarbon was commercially available at the time, ~~they~~ it had to be synthesized. The most convenient method of preparing these materials while allowing for tailorability is the hydrosilation of alkyl chains onto vinylPOSS™:

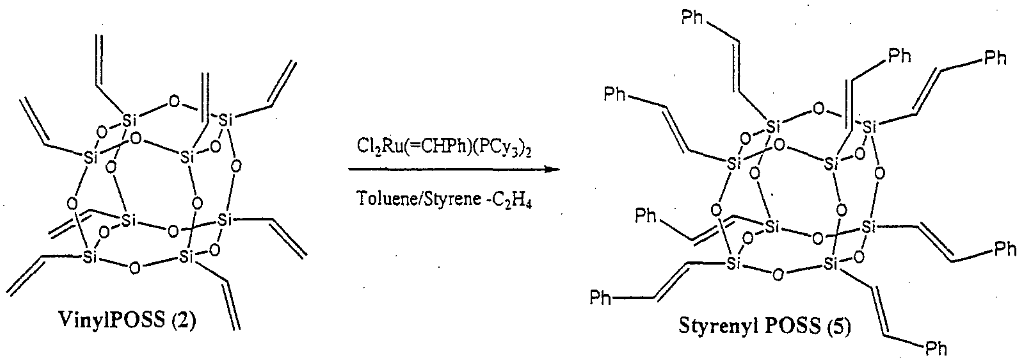


Octa-(Octyl$SiMe_2$)POSS™ (4) is one of the first well-defined POSS™ compounds that is a liquid at room temperature

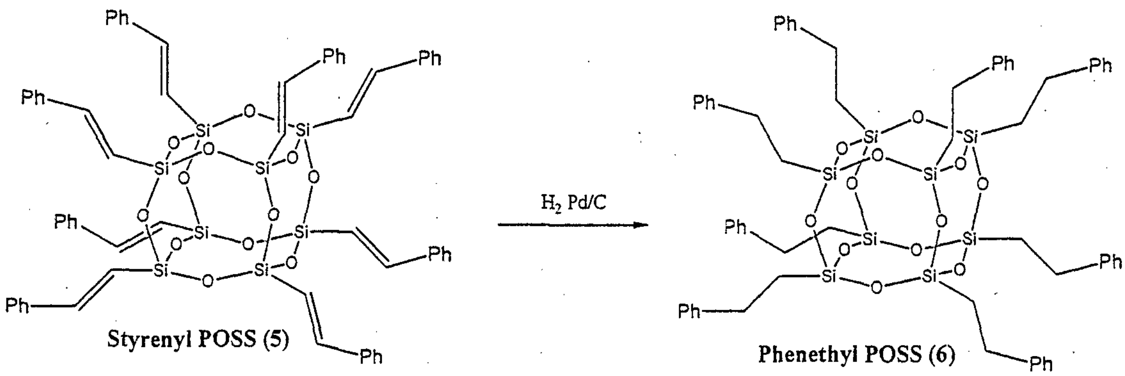
Cross Metathesis of POSS™

One class of polymers we wanted to investigate for the blends project is the class with aromatic functionalities. Examples of such polymers are polystyrene, BPA polycarbonate, polyester (PET, etc.), and SB rubber. At the time it was reasonable to believe that in order to blend POSS™ into a polymer with a high degree of dispersion, the organic side groups should be compatible with the polymer matrix (like dissolves like). Early attempts at blending with Phenyl$_8T_8$ led to mixed results. One of the problems with Phenyl$_8T_8$ is that it is a highly ordered crystalline solid, and these crystals have trouble breaking up and dispersing in the polymer matrix. To solve this problem, we had to develop other POSS™ compounds that contained aromatic groups. One convenient method to prepare these materials is by the cross metathesis reaction. Feher[4] first demonstrated the viability of cross metathesis technology involving POSS™ materials in 1998. This technology was utilized to synthesize Styrenyl POSS™ **5** (Styrenyl$_8T_8$) on a 200-gram scale. StyrenylPOSS™ is a white, crystalline solid with a melting temperature above 200 °C. Despite the steric crowding around the double bonds, they can still undergo reaction chemistry. For example, the double bonds of **5** are readily

oxidized with MCPBA to give stable epoxides that are dispersible in commercially available epoxies (Epon 828).



While the double bonds of StyrenylPOSS™ are accessible for reaction chemistry, they might present problems at higher temperature with unwanted reactivity. The easiest approach would be to hydrogenate the double bonds to give a completely saturated species and therefore a higher resistance to oxidation. To this end, $Phenethyl_8T_8$ (**6**) was synthesized by the hydrogenation of StyrenylPOSS™ using palladium on carbon as the hydrogenation catalyst. It is a colorless solid with a melting temperature of 74 °C.



Synthesis of POSS™-Polyolefin Blends

One of the potential uses for POSS™ in polymers is its use as a flame retardant, and the initial blending studies focused on polyethylene because of HDPE's commodity status. In the case of POSS™ oil **4**, it can be blended into HDPE using traditional blending techniques. The blended material has the same appearance as the unblended polymer. This material was tested for flame retardance, but was not effective because of the low percentage of silica in the POSS™ sample (20 wt. %). Another drawback with this material is that the hydrocarbon content of the POSS™ is rather high (~80%). POSS™ with higher silica content ~~are~~ is required and will be reported in due course.

Synthesis of POSS™-Polystyrene Blends

We wanted to undertake a more detailed study to see the dependency of the R group on solubility of POSS™ in a polymer. The polymer that was chosen was polystyrene. With polystyrene, we can add a diverse array of POSS™ molecules with varying R groups. In the study, we chose $cyclopentyl_8T_8$ (**1**), $vinyl_8T_8$ (**2**), $cyclopentyl_7T_8styryl$ (**3**), $Styrenyl_8T_8$ (5) and $Phenethyl_8T_8$ (**6**). Since we were casting films of 50% POSS™/50%

PS from thf solutions, the POSS™ needed to be soluble as well. Fortunately, these POSS™ molecules are indeed soluble in thf. The first blend looked at in this study is the mixture of cyclopentyl$_8$T$_8$ (1) and polystyrene. The film cast was opaque. The TEM (Figure 1) shows that there are large POSS™ crystallites that contain between 20K and 50K molecules with no apparent POSS™ in the polystyrene phase. Apparently the cyclopentyl groups are not compatible with the polystyrene matrix.

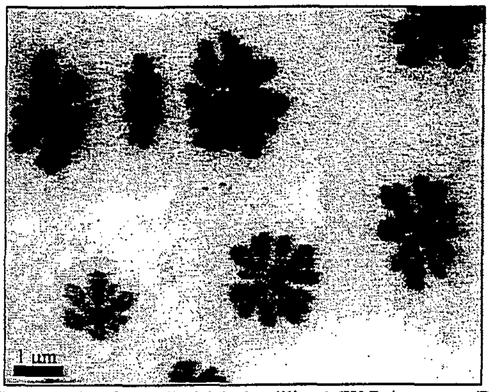


Figure 1. (cy-C_5H_9)$_8$T$_8$ (1) in 2 million MW Polystyrene (PS)

Figure 2. (vinyl)$_8$T$_8$ in 2 million MW Polystyrene (PS)

The second blend looked into for this study is the mixture of vinyl$_8$T$_8$ (2) and polystyrene. The film that was cast was also opaque. The TEM (Figure 2) shows that there is no apparent POSS™ in the polystyrene phase, although the crystallite size is smaller than the above blend with polystyrene and 1.

Upon the addition of one compatiblizing group on the POSS™ molecule, dramatic improvement in compatibility results. When Styryl-POSS™ (3) is cast with polystyrene, a less opaque film is obtained compared to both of the previous films. The TEM of this blend of Styryl-POSS™ (3) and polystyrene shows that crystallite size drops off dramatically after the replacement of only *one* incompatible cyclopentyl group with a more compatible styryl group (Figure 3).

When all eight incompatible groups are replaced by aromatic styrenyl groups and cast with polystyrene, an optically clear film is obtained. The TEM of this blend of Styrenyl$_8$T$_8$ (4) and polystyrene, shown in Figure 4, displays isolated polystyrene domains as well as a gray area that represents the POSS™-PS domain. The black dots in the TEM are believed to be POSS™ crystallites in the POSS™-PS phase that contain <100 POSS™ molecules. It is believed that the isolated polystyrene domains are a result of the solvent casting process and the high molecular weight of the polymer. This shows that we now have a POSS™ molecule that is miscible with the polystyrene phase. In

Figure 3. TEM of 50% Styryl-POSS™ in 2 million MW Polstyrene

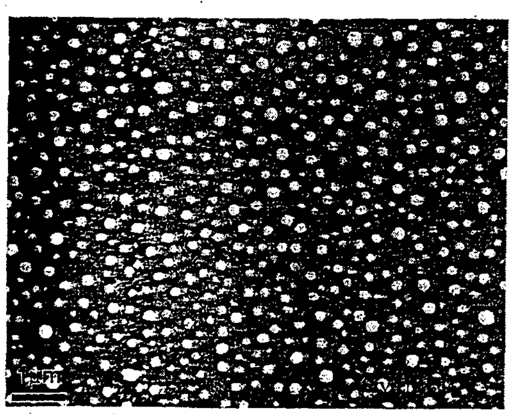


Figure4. (Styrenyl)$_8$T$_8$ in 2 million MW Polystyrene (PS)

addition to the miscibility observed with the styrenyl-POSS™ monomer in the polystyrene matrix, a 30% increase in the surface hardness of film compared to undoped styrene is observed.

In order to overcome the processing issues with styrenyl-POSS™ and to make a more oxidatively resistant additive, the double bonds of **5** were removed by hydrogenation to give phenethyl-POSS™ (**6**). The film cast with **6** and polystyrene is again optically clear. The TEM of this mixture (Figure 5) shows sample homogeneity across the sample with POSS™ rich domains in the POSS™-PS phase which contain <100 POSS™ molecules. An X-ray powder diffraction spectrum for this polymer shows no observable crystallinity attributable to PhenethylPOSS™. In addition, there is no observable transition for the melting of PhenethylPOSS™ in the sample, which is consistent with the lack of large crystalline domains of PhenethylPOSS™.

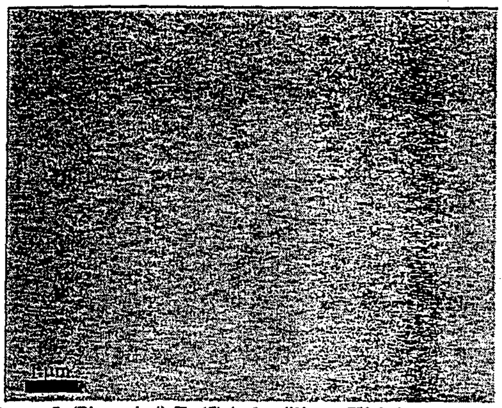


Figure 5. (Phenethyl)$_8$T$_8$ (5) in 2 million MW Polystyrene (PS)

With the information gleaned from this study, we decided to look into the blends of Phenethyl$_8$T$_8$ and other resins with aromatic groups. Instead of dissolving in thf and casting films (which is impractical on a larger scale), we used traditional melt blending techniques with a DACA twin-screw mixer. A representative sample of resin/POSS™ blends is ~~are~~ summarized in Table 1.

Table 1. Selected Data of POSS™/Polymer Blends

Resin	POSS Compound 10% loading	Processing Temp. °C	Appearance
Polystyrene	Phenethyl$_8$T$_8$	177	Clear
BPA polycarbonate	Phenethyl$_8$T$_8$	300	Clear
SB Rubber	Phenethyl$_8$T$_8$	100	Clear

Several other blends with varying loading were also made, and when the resin contained aromatic functionality and was ~~is~~ clear before blending with phenethylPOSS™, it was ~~is~~ clear after blending as well. One of the methods we use to check for performance enhancement is Dynamic Mechanical Thermal Analysis (DMTA). To utilize this technique, we prepared two samples; the first is polystyrene with 5 wt. % phenethylPOSS™ blended in, and the second is virgin polystyrene. Both materials have identical thermal histories (both mixed in the DACA for the same amount of time and pressed into films). When the POSS™ was mixed into the polystyrene, the load on the blender did not increase as in the case of usual fillers; in fact, the load decreased. This

phenomena may come in useful for difficult-to-process materials. Below in Figure 6 are DMTA traces for a DACA blend of 5 wt. % of phenethylPOSS™ in polystyrene and polystyrene with no POSS™ in the sample as a standard. As can be seen by comparing the traces, addition of phenethylPOSS™ into polystyrene at this low loading leads to a material with a slight decrease of T_g compared to the unblended polystyrene. This material may be useful ~~for use~~ as a flame retardant that does not seriously affect the mechanical properties of the base resin. Additional blends of phenethylPOSS™ in polystyrene are planned to see if this phenomenon holds at higher weight percentages of POSS™.

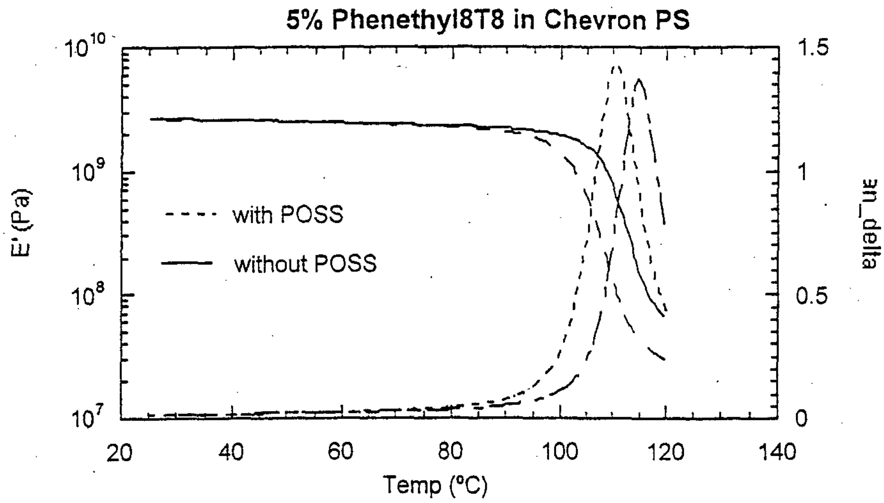


Figure 6. DMTA of Polystyrene and PS with 5 wt.% PhenethylPOSS™

Conclusions

We have demonstrated the ability to disperse polyhedral oligomeric silsesquioxanes into polystyrene. We have also shown that by altering the organic side groups of POSS™ compounds to a more compatible group, we can fully disperse the POSS™ molecules into high molecular weight polystyrene and, in the case StyrenylPOSS™/polystyrene film, an increase of 30% in the surface hardness is observed.

Future Work

One of the applications in which we are interested ~~in~~ is the use of POSS™ as a flame retardant. While vinyl$_8$T$_8$ is not miscible in polystyrene, a partially functionalized vinyl$_8$T$_8$ with aromatic groups should be. The concept of partial cross metathesis with vinyl$_8$T$_8$ and styrene has been proven, and future work will focus on blends of these POSS™ compounds. Another possibility is the use of vinyl$_n$T$_n$ as a reactive blendable with resins.

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